

# VAN DER WAALS INTERACTION FOR STRONGLY INTERACTING LIQUIDS

ANDREW DAS ARULSAMY

**ABSTRACT.** The origin of an attractive van der Waals (vdW) interaction between two identical neutral atoms is due to an approximately isotropic polarization, which has been solved exactly if the distance between the atoms is very large compared to atomic size. Therefore, the vdW interaction is always assumed to be long range by default. Here, we prove (i) the existence of a blue-shifting vdW interaction for both long and short distances, and (ii) the original vdW theory does not lead to an attractive interaction between two strongly interacting atoms with large non-isotropic polarization.

## 1. INTRODUCTION

The first van der Waals (vdW) macroscopic model was introduced by Derjaguin [1], while Lifshitz developed the comprehensive macroscopic vdW theory for solid objects by relating the long-range electromagnetic forces to the vdW interaction within the Green function and quantum field theory formalism [2]. Subsequently, exact expressions for spherical objects were derived by Langbein within the Lifshitz theory [3]. However, the vdW forces discussed therein are related to the interaction between macroscopic solid bodies. On the other hand, the well-known exact solution for the semiclassical two-atom system can be found in Ref. [4], while a more comprehensive quantum mechanical results were obtained by Chang [5] *via* the  $1/R$  multipole expansion. We will revisit this expansion later to point out what are the conditions that needed to be imposed so that the  $1/R$  multipole expansion is valid (given in the Sections, Further analyses I and II).

Even in this simple system, the attractive vdW interaction has always been a long-range type (for weakly interacting liquids), and there is no known result whether attractive vdW interaction can even exist at all for atoms polarized non-isotropically. Here, we prove that the attractive vdW interaction can indeed blue-shift for large non-isotropic (and asymmetric) polarization, and therefore, can be made to be significantly relevant even for short distances (shorter than the intermediate distances considered in Ref. [5]).

The motivation to revisit the vdW theory is due to its importance in biological and biochemical processes such that the blue-shifted vdW interaction could activate biochemical reactions [6]. Here, we will attempt to expose the existence of a stronger attractive interaction for strongly interacting atoms or molecules in a liquid phase. Such a stronger attraction is also important to investigate chemical reactions due to blue shifting hydrogen bonds [7] in the presence of directional polarization [8].

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Details on this blue-shifting hydrogen bonds are available here [9, 10, 11]. Here, we prove that the precise microscopic mechanism for the existence of this blue-shifting hydrogen bonds can be generalized to all atoms by means of blue-shifting vdW attraction. We also show how does this vdW interaction strength changes with different types of atoms. Here, we will prove (i) that there is a blue-shifting vdW attraction for short distances between two atoms that are asymmetrically polarized, and (ii) the original vdW theory does not lead to an attraction between two strongly interacting atoms with large non-isotropic polarization. We will address these two issues microscopically and analytically.

## 2. RENORMALIZED VDW ATTRACTIVE INTERACTION

The relevant Hamiltonian for the two-atom system (strictly neutral atoms, but with polarizable valence electrons) plotted schematically in Fig. 1 is given by [4]

$$(2.1) \quad \begin{aligned} H &= H_O + H_I, \quad H_O = \frac{p_1^2}{2m} + \frac{kr_1^2}{2} + \frac{p_2^2}{2m} + \frac{kr_2^2}{2}, \\ H_I &= \frac{1}{4\pi\epsilon_0} \left[ \frac{(e)(e)}{R} + \frac{(-e)(e)}{R+r_2} + \frac{(-e)(e)}{R-r_1} + \frac{(-e)(-e)}{R-r_1+r_2} \right], \end{aligned}$$

where  $p_{1,2}$  are the electrons momenta, and the ground state energy for the above Hamiltonian is (taking  $R \gg r_{1,2}$  and after some nontrivial substitutions) [4]

$$(2.2) \quad E = \frac{1}{2}\hbar \left[ \sqrt{\frac{k - (\epsilon^2/2\pi\epsilon_0 R^3)}{m}} + \sqrt{\frac{k + (\epsilon^2/2\pi\epsilon_0 R^3)}{m}} \right],$$

where  $m$  is the electron mass. Note here that  $\mathbf{r}_1$  and  $\mathbf{r}_2$  are indeed vectors, but we have aligned the atoms such that their electronic polarization are maximum along a straight line where  $\mathbf{r}_1 \rightarrow r_1$  and  $\mathbf{r}_2 \rightarrow r_2$ . We now prove why this alignment is valid for three-dimensional cases (imagine two polarizable spheres)—suppose  $\mathbf{r}_1$  (from sphere 1) is aligned along the  $x$  axis, so that  $|\mathbf{r}_1| = r_1$ . The induced polarization due to  $\mathbf{r}_1$  causes  $|\mathbf{r}_2| = r_2(\theta, \phi)$  where  $\theta < \pi/4$ ,  $\phi < \pi/4$ ,  $\theta$  is the angle in the  $xy$ -plane and  $\phi$  denotes the angle in the  $xz$ -plane. It is easy to verify that if  $\theta \geq \pi/4$  and  $\phi \geq \pi/4$ , then there is an additional induced polarization affecting  $|\mathbf{r}_2| = r_2(\theta, \phi)$ . If such a case exists, then we just need to take this additional polarization into account (that affects  $\mathbf{r}_2$ ), and realign  $\mathbf{r}_2$  (from sphere 2) with respect to this new  $\mathbf{r}'_1$ . In this second case,  $|\mathbf{r}'_1| = r'_1$  causes  $|\mathbf{r}'_2| = r'_2(\theta, \phi)$  where  $\theta < \pi/4$  and  $\phi < \pi/4$ . This means that,  $\theta$  and  $\phi$  remains the same such that  $\theta \in (0, \pi/4]$  and  $\phi \in (0, \pi/4]$ . For one-dimensional cases,  $\theta = 0 = \phi$ , while for a two-dimensional case, one has  $\theta \in (0, \pi/4]$  and  $\phi = 0$ .  $\square$

In Eq. (2.2),  $\hbar$  is the Planck constant divided by  $2\pi$ ,  $R$  is the distance between two neutral and identical atoms. The subscripts 1 and 2 refer to electron 1 and 2 bounded within nuclei 1 and 2, respectively. The ordinary Hamiltonian denoted by  $H_O$  consists of two kinetic energy terms, and two semiclassical harmonic-oscillator type electron-ion potential terms, and they are associated to two bounded valence electrons within their respective nuclei (see Fig. 1). The interaction Hamiltonian,  $H_I$  captures all the Coulomb interaction between the two atoms depicted in Fig. 1. Note that  $H_I$  does not consider the Coulomb forces within the atom (between the valence electrons and their respective nuclei), which have been taken into account by  $H_O$ .

Now, one can renormalize the interaction potential constant,  $k$  such that [12]

$$(2.3) \quad \tilde{k} = k \exp[\lambda\xi],$$

where  $\lambda = (12\pi\epsilon_0/e^2)a_B$ , in which,  $a_B$  is the Bohr radius of atomic hydrogen,  $e$  and  $\epsilon_0$  are the electron charge and the permittivity of free space, respectively. The above renormalization procedure is also related (exactly) to the Shankar renormalization technique [13, 14, 15]. Here,  $\xi$  is known as the energy spacing between any two energy levels, and it is also known as the ionization energy. Now the real value for  $\xi$  for a given quantum matter is unknown, and therefore, we will need to make use of an approximation. This approximation can be understood from the IET-Schrödinger equation [12],

$$(2.4) \quad i\hbar \frac{\partial \Psi(\mathbf{r}, t)}{\partial t} = \left[ -\frac{\hbar^2}{2m} \nabla^2 + V_{\text{IET}} \right] \Psi(\mathbf{r}, t) = H_{\text{IET}} \Psi(\mathbf{r}, t) = (E_0 \pm \xi) \Psi(\mathbf{r}, t),$$

where  $\hbar = h/2\pi$ ,  $h$  denotes the Planck constant and  $m$  is the mass of electron, and  $\Psi(\mathbf{r}, t)$  is the time-dependent many-body wave function. The eigenvalue,  $E_0 \pm \xi$  is the real (true and unique) energy levels for a given quantum system (for a given molecule). Here,  $E_0$  is a constant because it represents the energy level spacings at zero temperature, and in the absence of any external disturbances. On the other hand,  $\xi = \xi_{\text{matter}}^{\text{quantum}}$  is the so called ionization energy. Therefore, all we need to do now is to find a way to obtain  $\xi_{\text{matter}}^{\text{quantum}}$ .

Instead of finding a way to calculate  $\xi_{\text{matter}}^{\text{quantum}}$ , which is in itself an unsolved problem (since the invention quantum theory), we make use of the ionization energy approximation to approximate  $\xi_{\text{matter}}^{\text{quantum}}$ . This approximation hinges on this proportionality,

$$(2.5) \quad \xi_{\text{matter}}^{\text{quantum}} \propto \xi_{\text{atom}}^{\text{constituent}}.$$

As stated earlier,  $\xi_{\text{matter}}^{\text{quantum}}$  represents the real energy level spacings of a particular quantum system, and it can be regarded as a generalized electronic energy gap. This means that, in molecules,  $\xi_{\text{matter}}^{\text{quantum}}$  is the energy level spacing between an occupied level (in the highest occupied molecular orbital (HOMO)) and an empty level (in the lowest unoccupied molecular orbital (LUMO)). Using this approximation, we can now predict the changes to  $\xi_{\text{matter}}^{\text{quantum}}$  if we know  $\xi_{\text{atom}}^{\text{constituent}}$ . The values for  $\xi_{\text{atom}}^{\text{constituent}}$  can be readily obtained from the experimental atomic spectra. The ionization energy approximation becomes exact if the quantum matter are atoms or ions ( $\xi_{\text{matter}}^{\text{quantum}} = \xi_{\text{ion}}^{\text{atom}}$  from Eq. (2.5)). The approximation given in Eq. (2.5) has been proven—the indirect proof reads,  $H_{\text{IET}} \Psi(\mathbf{r}, t) = (E_0 \pm \xi_{\text{matter}}^{\text{quantum}}) \Psi(\mathbf{r}, t) \propto (E_0 \pm \xi_{\text{atom}}^{\text{constituent}}) \Psi(\mathbf{r}, t)$ , while the second formal proof is direct based on logic and the excitation probability of electrons and holes within the ionization energy based Fermi-Dirac statistics [12].

From here onwards, any variable found to wear a tilde implies a renormalized parameter. Subsequently,  $E$  can be written in the form (after making use of the series,  $\sqrt{1+x} = 1 + x/2 - x^2/8 + x^3/16 - \dots$ )

$$(2.6) \quad \begin{aligned} \tilde{E}(\xi) = & \frac{\hbar}{2} \left[ \left( 1 - \left( \frac{e^2}{2\pi\epsilon_0 R^3} \right) \frac{1}{2\tilde{k}} - \left( \frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \frac{1}{8\tilde{k}^2} - \dots \right) \right. \\ & \left. + \left( 1 + \left( \frac{e^2}{2\pi\epsilon_0 R^3} \right) \frac{1}{2\tilde{k}} - \left( \frac{e^2}{2\pi\epsilon_0 R^3} \right)^2 \frac{1}{8\tilde{k}^2} + \dots \right) \right] \sqrt{\frac{\tilde{k}}{m}}, \end{aligned}$$

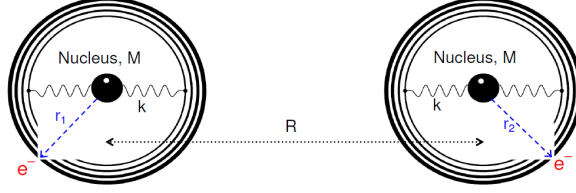


FIGURE 1. Two identical atomic system with discrete energy levels are sketched where  $r_{1,2}$ ,  $M$  and  $k$  denote the coordinate for the valence electrons,  $e^-$ , the ionic mass and the spring (interaction potential) constant, respectively. The discrete and quantized energy levels strictly imply non-free electrons. Here,  $R$  is the distance between those two nuclei, and  $M \gg m$  where  $m$  is the mass of a valence electron. We set the coordinate such that  $r_{1,2}$  and  $R$  are all on the  $x$ -axis where the charges are arranged in a straight horizontal line, in the following order,  $+ - + -$ . Negative charges correspond to the valence electrons from the left and right atoms, while the positive charges are from the respective nuclei. In the text, we also denote the left atom as atom 1, whereas atom 2 is to the right.

in which, we consider only the first three terms by imposing the condition,  $k \exp[\lambda \xi] \gg (e^2/2\pi\epsilon_0 R^3)$ , in other words  $(e^2/2\pi\epsilon_0 R^3)^n \tilde{k}^{-n} \approx 0$  for  $n \geq 4$  and  $n \in \mathbb{N}_{\text{even}}$  where  $\mathbb{N}_{\text{even}}$  is the set of even natural numbers. In addition,  $\tilde{\omega}_0 = \sqrt{\tilde{k}/m}$ . Subsequent algebraic rearrangements of Eq. (2.6), after subtracting  $\hbar\tilde{\omega}_0$  will lead us to

$$(2.7) \quad \tilde{E}(\xi) - \hbar\tilde{\omega}_0 = \tilde{V}_{\text{Waals}}^{\text{std}}(\xi) = \left\{ -\frac{\hbar}{8m^2\omega_0^3} \left( \frac{e^2}{2\pi\epsilon_0} \right)^2 \frac{1}{R^6} \right\} \exp \left[ -\frac{3}{2}\lambda\xi \right].$$

This is the standard vdW interaction energy in its renormalized form (due to the renormalizing factor (renormalizer for short),  $\exp[-(3/2)\lambda\xi]$ ), and note the popular vdW factor,  $1/R^6$ . The original (unrenormalized) vdW formula is given in the curly bracket.

The term,  $\hbar\tilde{\omega}_0$  is the renormalized ground state energy ( $\tilde{E}(\xi)$ ) when  $H_1 = 0$  (in the absence of Coulomb interactions between charges from different atoms or molecules). One can observe the correct trend from Eq. (2.7), in which, for a given  $R$ , when  $\xi$  shoots to infinity (valence electrons with zero polarization),  $\tilde{V}_{\text{Waals}}^{\text{std}}(\xi) \rightarrow 0$ , as it should be. In contrast,  $\tilde{V}_{\text{Waals}}^{\text{std}}(\xi) \rightarrow \text{maximum}$ , if  $\xi$  obtains an allowable minimum value. Note here that taking  $\xi = 0$  is physically not acceptable as this means that the valence electrons are not bound to their respective nuclei, and they are free. For the same reason, after replacing  $\lambda = 1/k_B T$  where  $k_B$  is the Boltzmann constant [16], one cannot take the temperature of a system to infinity because physically (or chemically), this does not make any sense either, as there can be any number of emergent phases due to quantum phase transitions for any finite temperature [17].

### 3. STRONGER VDW INTERACTION DUE TO LARGE NON-ISOTROPIC POLARIZATION

In any case, the above standard attractive interaction (see Eq. (2.7)) is not strong enough because the polarization is either small or, if the polarization is large, then it is approximately isotropic (see Fig. 2(A)) because the atoms are weakly interacting. In the case of strongly interacting atomic-system, a larger induced non-isotropic polarization is obtainable (see Fig. 2(B)). Here, Fig. 2(A) depicts a weakly interacting system with an isotropically polarized atom, while Fig. 2(B) and (C) depict two types of strongly interacting liquids with non-isotropic polarization. To induce such a non-isotropic polarization, we need a stronger interaction between these atoms such that the condition,  $R \gg r$  is not violated (to make sure Eq. (2.2) is still valid). In other words, we need the non-isotropic polarization to be large enough (with small  $\xi$ ) to give  $k \exp[\lambda\xi] \approx (e^2/2\pi\epsilon_0 R^3)$ , not  $k \exp[\lambda\xi] \gg e^2/2\pi\epsilon_0 R^3$ . After making use of this new condition, we can rewrite Eq. (2.2) to obtain (subject to the renormalization procedure developed in Ref. [12])

$$(3.1) \quad \tilde{E}(\xi) - \hbar\tilde{\omega}_0 = \tilde{V}_{\text{Waals}}(\xi) = \frac{1}{2}\hbar \left[ \sqrt{\frac{2\tilde{k}}{m}} \right] - \hbar\tilde{\omega}_0.$$

Eq. (3.1) can be rearranged to arrive at

$$(3.2) \quad V_{\text{Waals}}(R) = \left[ \frac{\hbar^2 e^2}{2m\pi\epsilon_0} \right]^{\frac{1}{2}} \left( \frac{1}{\sqrt{2}} - 1 \right) \frac{1}{R^{3/2}},$$

$$(3.3) \quad \tilde{V}_{\text{Waals}}(\xi) = \hbar\omega_0 \left( \frac{1}{\sqrt{2}} - 1 \right) \exp \left[ \frac{1}{2} \lambda \xi \right],$$

by using  $\tilde{k} = (e^2/2\pi\epsilon_0 R^3)$  interchangeably.

Obviously,  $V_{\text{Waals}}(R)$  and  $\tilde{V}_{\text{Waals}}(\xi)$  are negative guaranteed by the inequality  $1/\sqrt{2} - 1 < 0$ , hence these interactions are always attractive, while the proportionality,  $V_{\text{Waals}}(R) \propto 1/R^{3/2}$  implies it is of a stronger-type compared to the renormalized standard vdW interaction,  $\tilde{V}_{\text{Waals}}^{\text{std}}(\xi) \propto 1/R^6$  (see Fig. 1). It is worth noting that the proportionality  $\tilde{V}_{\text{Waals}} \propto 1/R^{3/2}$  is identical to the vdW interaction energies derived for two different geometric conditions [18, 19]. In particular, the relevant geometric conditions are (a) two infinite-length cylinders with radii  $r_1$  and  $r_2$ , separated by  $R$ , and (b) a cylinder (radius  $r_1$  and with infinite length) separated from a two-dimensional sheet (negligible thickness but with infinite length and width) at a distance  $R$ . Contrary to Eq. (3.2), both (a) and (b) must satisfy the condition,  $R \ll r_{1,2}$ , in which, these classical objects are very close to each other [19]. In contrast, Eqs. (3.2) and (3.3) are for two spherical quantum objects (see Fig. 1) that satisfy conditions,  $R \gg r_{1,2}$  and  $k \exp[\lambda\xi] \approx (e^2/2\pi\epsilon_0 R^3)$  (large polarization or weakly bound valence electrons). This large polarization will give rise to a non-isotropic polarization in the presence of strong interactions between atoms.

However, the imposed condition  $R \gg r_{1,2}$  does not in any way, implies Eq. (3.3) is inapplicable for any  $R$  other than  $R \gg r_{1,2}$ . For example, what Eq. (3.3) tells us is that for a given  $R$  such that  $R \gg r_{1,2}$ , if  $\xi$  is large, then one obtains a large attractive interaction. Now, the only way to change the value of  $\xi$  is to change the type of atoms because each atom has a unique set of ionization energies or energy

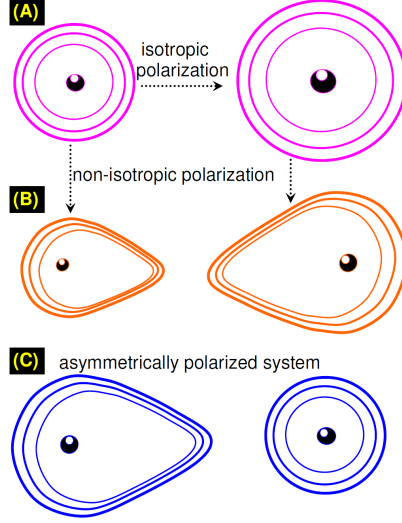


FIGURE 2. We define here the different types of polarizations discussed in the text. The sizes and shapes of the sketches are not to scale. The nuclei are at the center, while the lines represent the energy-levels, similar to Fig. 1. (A) The atom on the left is prior to polarization. After intense laser or at a higher temperature, the atom is polarized isotropically as we have sketched on the right-hand side. The two atoms sketched in (A) can also be non-isotropically polarized as sketched in (B), if and only if these two atoms interact strongly. Therefore, non-isotropic polarization is an induced polarization. This is often the case for strongly interacting liquids such that there exists an effective electron-electron Coulomb repulsion leading to a repulsion between these atoms. Apart from that, (C) asymmetric polarization can also occur if one of the atom is highly polarizable, while the other atom is the least polarizable one, which will give rise to an effective attractive interaction. Again, this attraction is only valid for strongly interacting liquids. However, if these two atoms interact weakly, then they are approximately isotropically polarized (regardless whether the polarization is large or small), giving rise to the standard vdW attractive interaction for  $R > r_1 + r_2$ . Here,  $R$  is the internuclear distance, while  $r_1$  and  $r_2$  denote the radii of the two isotropically polarized atoms. Here, Fig. 2 contains two-dimensional diagrams for clarity, but their analyses apply regardless whether a given system is one-, two- or three-dimensional.

level spacings. Therefore, when we extrapolate this scenario for any  $R$  such that  $R \geq r_1 + r_2$ , then such an extrapolation does not technically and physically change the effect of the renormalizer or  $\xi$ . In other words, large  $\xi$  still gives rise to large attractive vdW interaction, regardless whether the atoms are close to each other or far apart.

Unfortunately, Eq. (3.2) does not provide any new physical insight other than, that it is stronger than the original vdW interaction. Whereas, Eq. (3.3) is indeed a function of the microscopic variable,  $\xi$ , but physically not yet appropriate because Eq. (3.3) does not allow large non-isotropic polarization effect—the repulsive interaction between the non-isotropically polarized electrons from two identical atoms separated by  $R$ , will give rise to an effective repulsion, not an attractive interaction (see Fig. 2(B)). As a consequence, Eq. (3.3) certainly cannot lead to a stronger vdW attraction for large non-isotropic polarization, due to the  $e$ - $e$  repulsion between non-isotropically polarized atoms.

Moreover, having understood Eq. (2.7), Eq. (3.3) should look downright disturbing physically since  $\tilde{V}_{\text{Waals}}(\xi) \propto \sqrt{k} \exp[(1/2)\lambda\xi]$ : note the missing negative sign in the renormalizer. In other words, large vdW interaction energy is obtained only if the system is least polarizable, that seems to violate Eq. (2.7). But this is a false alarm, because if we look closely, it is neither surprising nor physically incorrect. The moment we allow large non-isotropic polarization with a new condition,  $k \exp[\lambda\xi] \approx (e^2/2\pi\epsilon_0 R^3)$ , the attractive interaction must now overcome the stronger repulsive electron-electron ( $e$ - $e$ ) Coulomb interaction ( $V_{\text{Coulomb}}^{e-e}$ ) due to non-isotropically polarized electrons. Therefore, the attractive interaction is only possible if the situation is reversed (compared to Eq. (2.7)), in such a way that increasing  $\xi$  (decreasing polarization) is favored for a maximum vdW attractive interaction ( $\tilde{V}_{\text{Waals}}(\xi)$ ), as it should be, to avoid the above Coulomb repulsion due to non-isotropic electronic polarization. This means that  $\tilde{V}_{\text{Waals}}(\xi) \rightarrow \text{maximum}$  when  $\xi$  obtains a maximum allowable value, or a minimum polarization.

Here, the minimum allowable polarization implies the minimum value is large enough, but not larger, so as not to activate the repulsive  $e$ - $e$  Coulomb interaction between the non-isotropically polarized atoms. In other words, we require  $V_{\text{Coulomb}}^{e-e} + \tilde{V}_{\text{Waals}}(\xi) < 0$ . As such, we can understand the negative sign in the renormalizer of Eq. (2.7) exists entirely due to the approximation originating from the condition,  $k \exp[\lambda\xi] \gg (e^2/2\pi\epsilon_0 R^3)$ , which allows us to invoke the solution in series, as stated earlier. In particular,  $k \exp[\lambda\xi] \gg (e^2/2\pi\epsilon_0 R^3)$  indirectly imposes the least polarizability (large  $\xi$ ) condition into the system. On the other hand, in Eq. (3.3), the least polarizability is directly captured via the renormalizer,  $\exp[(1/2)\lambda\xi]$ . Thus, even though at first we thought that we have successfully incorporated the large non-isotropic polarization effect by replacing  $k \exp[\lambda\xi] \gg (e^2/2\pi\epsilon_0 R^3)$  with  $k \exp[\lambda\xi] \approx (e^2/2\pi\epsilon_0 R^3)$ , but it turns out that we are back to square one, with an additional condition,  $V_{\text{Coulomb}}^{e-e} + \tilde{V}_{\text{Waals}}(\xi) < 0$ .

As a consequence, we have actually proven that the attractive vdW interaction cannot exist for a system consists of two highly non-isotropically polarizable atoms (due to strong interaction), for as long as the  $e$ - $e$  Coulomb repulsion between these non-isotropically polarized atoms is large. In fact, the existence and importance of  $V_{\text{Coulomb}}^{e-e}$  between any two highly non-isotropically polarizable entities has been analytically proven and discussed in Refs. [20, 21, 22]. Rightly so, the effect of non-isotropic polarization, induced by strongly interacting atoms, which gives rise to the  $e$ - $e$  repulsive interaction ( $V_{\text{Coulomb}}^{e-e}$ ) has been neglected in the standard (for both renormalized and original) vdW formula, given in Eq. (2.7).

Nevertheless, Eq. (3.2), which allows stronger vdW attractive interaction needs to be made compatible with Eq. (3.3) in the presence of large non-isotropic polarization. In order to do so, we need to do something to counter the repulsive

effect coming from  $V_{\text{Coulomb}}^{e-e}$ . We know Eq. (3.3) requires both atoms to be least polarizable such that the nuclei of atom 1 (left-hand side (l.h.s) of Fig. 1) attracts the valence electron of atom 2 (right-hand side (r.h.s) of Fig. 1), and vice versa, thus Eq. (3.3) cannot lead to a stronger vdW attraction.

However, the strength of this attraction can be greatly enhanced if the polarizabilities of these two atoms are made to be strongly asymmetric (see Fig. 2(C)), *i.e.*, these atoms are strongly interacting. Meaning, one atom is non-isotropically polarized in the presence of another. In particular, if one of the atoms has large  $\xi$ , while the other has small  $\xi$  ( $\xi_{\text{l.h.s}} < \xi_{\text{r.h.s}}$ ) then this will guarantee the existence of  $V_{\text{Coulomb}}^{e-\text{ion}} + \tilde{V}_{\text{Waals}}(\xi) < 0$  because  $V_{\text{Coulomb}}^{e-\text{ion}}$  is also negative by definition. In this case, the electron-ion (e-ion) Coulomb attraction ( $V_{\text{Coulomb}}^{e-\text{ion}}$ ) is between the polarized valence electron of atom 1 (easily polarizable) and the nuclei of atom 2 (difficult to be polarized). Therefore, to justify the stronger vdW attraction given in Eq. (3.2), we require asymmetric polarizabilities between two atoms with strong interactions (see Fig. 2(C)). In this case, an asymmetric-polarization can be properly introduced into Eq. (3.3) to obtain

$$(3.4) \quad \tilde{V}'_{\text{Waals}}(\xi) = V_{\text{Coulomb}}^{e-\text{ion}} + \frac{1}{2} \tilde{V}_{\text{Waals}}(\xi).$$

Equation (3.4) is the one that correctly corresponds to Eq. (3.2) in the presence of large asymmetric polarization (see Fig. 2(C)). The second term on the r.h.s of Eq. (3.4) represents the effect of two identical and weakly interacting atoms coming face-to-face (see Fig. 1), hence the factor 1/2. Both atoms in Fig. 1 are least polarizable (weakly interacting), and they affect each other equally with approximately isotropic polarization. While,  $V_{\text{Coulomb}}^{e-\text{ion}}$  is defined as the interaction between the polarized electron of an easily-polarizable atom and the nuclei of the least polarizable nearest-neighbor atom. Therefore, we do not need to include the factor 1/2 in  $V_{\text{Coulomb}}^{e-\text{ion}}$  due to its definition given above, in which the induced non-isotropic polarization is unidirectional, from the polarized valence electron of a strongly polarizable atom, to the nuclei of the least polarizable atom.

In the absence of renormalization, the new condition reads  $k \approx (e^2/2\pi\epsilon_0 R^3)$ , and one obtains an exact copy of Eq. (3.2) for  $V_{\text{Waals}}(R)$  and

$$(3.5) \quad V_{\text{Waals}}(k) = \hbar \sqrt{\frac{k}{m}} \left( \frac{1}{\sqrt{2}} - 1 \right).$$

Here, Eq. (3.5) physically correctly captures the same effect as Eq. (3.3). In particular, for a given separation  $R$ , large  $k$  implies small polarization, which is exactly identical to large  $\xi$  that causes small polarization. Hence, two least polarizable atoms (weakly interacting) can give rise to the standard vdW attractive interaction, for instance, when  $k \rightarrow \text{maximum}$  (from Eq. (3.5)), or  $\xi \rightarrow \text{maximum}$  (from Eq. (3.3)) then both  $V_{\text{Waals}}(k)$  and  $\tilde{V}_{\text{Waals}}(\xi)$  increase to a maximum value due to zilch Coulomb repulsion between the polarized electrons (isotropically polarized atoms). As stated earlier, Eq. (3.2) is independent of any microscopic variable (that can be related to the atomic structure), and as such it is not useful, except it correctly predicts the inverse proportionality between  $V_{\text{Waals}}$  and  $R^{3/2}$ . On the other hand, the changes in  $k$  (from Eq. (3.5)) is arbitrary, for example, we will never know how to implement the changes in  $k$  accordingly for different atoms in a given system. In contrast, and as proven earlier, only Eqs. (3.3) and (3.4) give us the option to accurately extract the microscopic information on two competing



interactions, between the vdW attraction and the  $e$ - $e$  Coulomb repulsion (due to non-isotropically polarized atoms) simultaneously, for strongly interacting atoms (*via*  $\xi$ ).

#### 4. FURTHER ANALYSES I

Equation (3.2) is shown to vary as  $1/R^{3/2}$ , and this stronger vdW attraction can only be understood by adding an attractive Coulomb interaction (due to asymmetric polarization between two strongly interacting atoms) to the standard vdW attraction (Eq. (2.7)). Therefore, due to this added Coulomb attraction, one cannot obtain Eq. (3.2) using the  $1/R$  expansion since each individual energy term in this expansion represents a specific interaction (Coulomb, dipole, quadrupole, and so on) without any additional interaction (that gives rise to non-isotropic polarization) added to  $1/R$  expansion [5]. Meaning, each specific interaction is determined by a specific  $m$  and varies as  $1/R^m$  where  $m = 1, 2, \dots$ , which is applicable for weakly interacting liquids. Recall here that a weakly interacting system means there will be no induced non-isotropic polarization, even though these atoms can have large isotropic polarization due to intense laser. To understand this point, we derive Eq. (2.7) using the second-order perturbation theory (the first-order energy is zero) [4]. The renormalized second-order energy

$$(4.1) \quad \tilde{E}_s^{(2)} = \left| -\frac{e^2}{2\pi\epsilon_0 R^3} \right|^2 \sum_{s \neq t}^{\infty} \frac{|\langle \varphi_t^{(0)}(1) | r_1 | \varphi_s^{(0)}(1) \rangle|^2 |\langle \varphi_t^{(0)}(2) | r_2 | \varphi_s^{(0)}(2) \rangle|^2}{[\tilde{E}_s^{(0)}(1) - \tilde{E}_t^{(0)}(1)] + [\tilde{E}_s^{(0)}(2) - \tilde{E}_t^{(0)}(2)]},$$

where (1) and (2) refer to atom 1 and 2 (see Fig. 1), while the subscripts,  $s$  and  $t$  denote the ground and excited eigenvalues ( $\tilde{E}_{s,t}$ ) and eigenstates ( $\varphi_{s,t}$ ), respectively. Moreover,

$$(4.2) \quad H_I \approx -\frac{e^2 r_1 r_2}{2\pi\epsilon_0 R^3},$$

after taking  $R \gg r_{1,2}$ . We first note

$$(4.3) \quad \tilde{E}_s^{(0)}(1) - \tilde{E}_t^{(0)}(1) + \tilde{E}_s^{(0)}(2) - \tilde{E}_t^{(0)}(2) = 2 \left[ \frac{1}{2} \hbar \tilde{\omega}_0 - \frac{3}{2} \hbar \tilde{\omega}_0 \right],$$

where  $(1/2)\hbar\tilde{\omega}_0 > 0$  is the ground-state eigenvalue, while  $(3/2)\hbar\tilde{\omega}_0 > 0$  is the first excited state eigenvalue for the harmonic oscillator-like two atomic system sketched in Fig. 1. Subsequently, using Eq. (4.3) and

$$(4.4) \quad |\langle \varphi_t^{(0)}(1) | r_1 | \varphi_s^{(0)}(1) \rangle|^2 |\langle \varphi_t^{(0)}(2) | r_2 | \varphi_s^{(0)}(2) \rangle|^2 = \left[ \frac{\hbar}{2m\tilde{\omega}_0} \right]^2,$$

we can derive Eq. (2.7) from Eq. (4.1) following Griffiths [4]—the renormalization procedure introduced here does not disturb the derivation in any way. As predicted earlier,  $\tilde{E}_s^{(2)} \propto 1/R^6$ , and is always negative determined entirely by the eigenvalue-denominator (ground state eigenvalue – excited state eigenvalue =  $-2\hbar\tilde{\omega}_0$ ) in Eq. (4.3). The numerator in Eq. (4.1) is positive-definite. Interestingly, the same conclusions (without renormalization) can be obtained from Ref. [5]. For example, the coefficient  $C_6$  [see Eq. (4.3) in Ref. [5]] represents the vdW attraction, and is always negative due to  $\epsilon_a(k_a) - \epsilon_a(k'_a) + \epsilon_b(k_b) - \epsilon_b(k'_b) < 0$  because  $\epsilon_{a,b}(k_{a,b}, k'_{a,b}) < 0$ ,  $|\epsilon_a(k'_a)| < |\epsilon_a(k_a)|$  and  $|\epsilon_b(k'_b)| < |\epsilon_b(k_b)|$ . Here,  $a$  and  $b$  denote

atom 1 and 2, respectively,  $k_{a,b}$  and  $k'_{a,b}$  represent both the principal and the angular momentum quantum numbers such that  $k_{a,b} \neq k'_{a,b}$ , while  $\epsilon_{a,b}$  are the respective eigenvalues.

To understand the above inequalities, assume  $a$  and  $b$  are two hydrogen atoms, and therefore,  $\epsilon_a(k_a)$  and  $\epsilon_b(k_b)$  are the ground-state eigenvalues for these atomic hydrogen, respectively, while  $\epsilon_a(k'_a)$  and  $\epsilon_b(k'_b)$  are the respective excited-state eigenvalues for hydrogen atoms. Since,  $E_1^{\text{ground}} = -13.6 \text{ eV} = \epsilon_a(k_a) = \epsilon_b(k_b)$ ,  $E_2^{\text{excited}} = -3.4 \text{ eV} = \epsilon_a(k'_a) = \epsilon_b(k'_b)$ , then you can immediately see why the denominator [in Eq. (4.6) of Ref. [5]] is always negative (as predicted earlier) for as long as the polarization is from a lower energy level (strongly bounded electron) to a higher energy level (weakly bounded electron).

Add to that,  $C_6 \propto 1/R^6$  originates from the interaction potential operator,  $V_3 \propto 1/R^3$  [see Eqs. (2.13) and (4.3) in Ref. [5]]. In our atomic system, we had  $H_1 \propto -1/R^3$  [see Eq. (4.2)]. Importantly, regardless whether  $V_3$  is negative or positive,  $C_6$  is guaranteed to be negative due to the eigenvalue-inequalities given above, and note that  $|\langle \dots | \pm V_3 | \dots \rangle|^2 \propto 1/R^6$ , which is positive-definite. As anticipated,  $V_3$  is a specific interaction potential ( $\mathfrak{m} = 3$ ), which was identified to give the vdW attraction without any additional induced non-isotropic polarization added to  $V_3$ . Therefore, similar to Eq. (2.7),  $V_3$  excludes the  $e$ - $e$  Coulomb repulsion in the presence of large non-isotropic polarization, both in the ground and excited states or in the mixed states. To those who are still not convinced, read the following analyses.

## 5. FURTHER ANALYSES II

The large  $e$ - $e$  repulsion due to large non-isotropic polarization (see Fig. 2(B)) has been excluded by invoking certain initial conditions used in Ref. [5] to write the potential,

$$(5.1) \quad V = \sum_{\mathfrak{m}=3}^{\infty} \frac{V_{\mathfrak{m}}}{R^{\mathfrak{m}}}.$$

The initial conditions were  $R > r_a + r_b$  such that most of the charges are distributed within an atomic or a molecular radius. This means that the allowable polarization is either small or increase isotropically (see Fig. 2(A)). Isotropically increasing polarization implies that the amount of increased polarization is essentially identical in all physical directions, namely, in  $x$ ,  $y$  and  $z$  axes. Now, these conditions need to be imposed so that Eq. (2.14) in Ref. [5] is valid. Rightly so, Chang has correctly invoked the above conditions even for large atomic or molecular polarization such that the amount of increased polarization is three-dimensionally isotropic. This in turn means that the systems studied there were for weakly interacting atoms or molecules. If the atoms or molecules are strongly interacting, then any polarization that increased isotropically has got to be invalid. In addition, the condition that requires the polarization to increase isotropically cannot hold for  $R \approx r_a + r_b$ .

Hence, what we have proven earlier is that isotropic polarization is inapplicable for  $R \approx r_a + r_b$  (for small internuclear distances) because we need to take the non-isotropic polarization effect into account, which has been included in our formalism [see the first term in Eq. (3.4)]. Moreover, one should also note that the isotropic polarization is not applicable for strongly interacting liquids, even if  $R > r_a + r_b$ . Thus, Eq. (3.4) is derived for strongly interacting liquids that allow asymmetric

polarization for  $R > r_a + r_b$  (see Fig. 2(C)). In contrast, isotropic polarization can only occur for systems that are weakly interacting and  $R > r_a + r_b$ . It is physically incorrect to enforce isotropic polarization for  $R \approx r_a + r_b$  or for strongly interacting liquids. In particular, for strongly interacting liquids with  $R \geq r_a + r_b$ , there will definitely be a significant amount of induced non-isotropic polarization on one atom or molecule that is caused by its neighboring atoms or molecules, which then gives rise to this strong asymmetric polarization. This is what we have addressed in this paper when we derived Eq. (3.4).

You may correctly wonder if there is an effective  $e$ - $e$  Coulomb repulsion between two isotropically polarized atoms or molecules. The effective repulsion will only be activated when the electrons in both atoms or molecules are polarized non-isotropically in the presence of strong interaction between these atoms or molecules, and/or when  $R \approx r_a + r_b$ . For example, atoms or molecules will be isotropically polarized in the gas-phase, if these atoms or molecules are weakly interacting in the presence of high temperature or intense laser. This isotropic polarization can be large. In this case, Eqs. (2.1) and (2.2) are applicable where one just starts with a new set of radii for atom 1 and 2, and again obtains Eq. (2.7). The new set of radii are larger than the original radii because the electrons are now polarized isotropically (see Fig. 2(A)). In fact, one can go on and improve Eq. (2.7) by incorporating other leading terms due to spin-orbit coupling and quadrupole-quadrupole interaction as carried out by Chang [5]. But this additional effects cannot induce the  $e$ - $e$  Coulomb repulsion, which is due to non-isotropic polarization, which occurs exclusively when there is a strong interaction between atoms or molecules or when the average internuclear distance,  $R \approx r_a + r_b$  (that eventually will induce the strong interaction).

Now, you should not be carried away into thinking that the standard vdW theory can handle non-isotropically polarized atoms or molecules just because it has incorporated other leading terms, namely,  $1/R^5$  (quadrupole-quadrupole) and  $1/R^3$  (magnetic interaction or due to spin-orbit coupling). These terms do improve the potential given in Eq. (5.1) by incorporating the above stated physical mechanisms, and can be used to improve Eq. (4.2), but they (the other leading terms) do not cause the  $e$ - $e$  Coulomb repulsion to exist. For example, these other leading terms are there to improve the equation for  $C_6$  or Eq. (2.7) by incorporating the appropriate correction terms such that each term represents a specific physical effect, namely,  $1/R^3$  represents magnetic interaction, whereas  $1/R^5$  is due to quadrupole-quadrupole interaction. In this case, the Coulomb repulsion is not a correction term, but originates from the  $e$ - $e$  repulsion due to polarized electrons. This means that, the first term in Eq. (3.4) is the leading term that represents the asymmetric polarization, and is responsible for the stronger vdW attraction in strongly interacting liquids. In particular, the above  $e$ - $e$  Coulomb repulsion, which is due to the large non-isotropic polarization, caused by the strongly interacting atoms or molecules, can only be overcome by the first term in Eq. (3.4). As a matter of fact, Eq. (2.14) in Ref. [5] has been enforced to make sure that the standard vdW theory presented in Ref. [5] is for isotropic polarizations, which does not take large non-isotropic polarization effect into account. For example, see the spherical harmonics given on page 139 in Ref. [4] and Eq. (2.15) in Ref. [5] to observe the expansion for  $V_m$  that is isotropic by definition, which has been enforced in Ref. [5]. For example, the standard vdW theory given in Ref. [5] is valid for weakly interacting system and for

$R > r_a + r_b$  such that the polarizations are (assumed to be) approximately isotropic. On the other hand, the vdW theory with asymmetric polarization developed here is valid for strongly interacting liquids, and for  $R \geq r_a + r_b$ .

In summary, a new van der Waals (vdW) interaction of a stronger type is proven to exist by generalizing the original vdW interaction, which is also related to Hermansson blue-shifting hydrogen bonds. The generalization includes three types of polarizations between two atoms, namely, isotropic, anisotropic and asymmetric polarizations. We show that an isotropic polarization is only valid for  $R \gg 2r$  ( $r = r_a = r_b$ ), which is a well known result within the original vdW theory. But the other two polarizations (anisotropic and asymmetric) are shown to be valid for all  $R$ . Recall here that  $R$  is the internuclear distance between two atoms, while  $r$  is the atomic radius for two identical atoms. Using the above generalization, we went on to explain why and how the original vdW attraction does not lead to an attractive interaction between two highly polarizable atoms due to large Coulomb repulsion between polarized electrons. This explains why  $R \gg r$  is a necessary condition for systems with isotropic polarizations, in accordance with the original vdW formalism. However, for  $R \approx 2r$ , the two atomic system should be considered as strongly interacting, giving rise to an anisotropic or an asymmetric polarization. In these cases, there is no requirement on  $R$  such that these polarizations are valid for any  $R$ . Hence, these two (anisotropic and asymmetric) polarizations, which are not captured by the standard vdW, have been proven to exist, which could lead us to understand the (bio)chemical reactions down to an electronic level.

## 6. CONCLUSIONS

We have formally proven the limitation in the original vdW formalism, in which, the Coulomb repulsion between polarized electrons has been neglected. In particular, the Coulomb repulsion is deliberately avoided by requiring small polarization, which has been implicitly embedded into the original formalism by requiring the interaction potential constant ( $k$ ) to be much greater than the Coulomb interaction between atoms (molecules). Or, by imposing a large isotropic polarization by invoking spherical harmonics. After taking the large non-isotropic polarization effect into account, we managed to obtain a new vdW formula of a stronger type, which is proportional to  $1/R^{3/2}$ . However, the new formalism also leads to a formula that is proportional to  $\exp[\lambda\xi]$  where  $\xi$  is the energy level spacing of a given molecule or system. Here, large  $\xi$  means large  $k$ , in accordance with the original vdW theory. Therefore, large non-isotropic polarization does not favor large attractive interaction at all, because of the  $e-e$  Coulomb repulsion effect (due to polarized electrons).

To overcome this intrinsic problem, large asymmetric polarization between two interacting molecules was invoked to prove the existence of a blue-shifting vdW interaction, in which, the above repulsion has been physically converted into a Coulomb attraction *via* an asymmetric polarization. For example, the attraction between the polarized electrons (of an easily non-isotropically polarizable atom) and a nearest neighbor nucleus (of the least polarizable atom) gives rise to this asymmetric polarization. This means that, the large vdW interaction (due to  $1/R^{3/2}$ ) can be justified with the large asymmetric polarization effect. Therefore, there exists a blue-shifting attractive vdW interaction between two strongly interacting atoms if they are polarized asymmetrically such that one of the atom or molecule

is non-isotropically polarized due to interaction with its nearest least-polarizable neighbor.

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*E-mail address:* sadwerdna@gmail.com

CONDENSED MATTER GROUP, DIVISION OF INTERDISCIPLINARY SCIENCE, F-02-08 KETUMBAR HILL, JALAN KETUMBAR, 56100 KUALA-LUMPUR, MALAYSIA